Selenium Uptake by Western Mountain Aster at Wooley Valley Unit 4 Waste Rock Dump

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Abstract

Phosphate mine waste rock dumps and associated vegetative cover in southeast Idaho contain elevated levels of Se from Permian Phosphoria Formation shale discarded during mining operations. Selenium accumulator plant species have potential to remove excess levels of plant-available Se from the rooting zone on waste rock dumps, but these species are rarely found on these dumps. The only frequently observed (but still a minor vegetative component) Se-accumulator species on waste rock dumps, western mountain aster, was found to accumulate Se concentrations as much as two orders of magnitude greater than the main waste rock dump re-vegetation species western wheatgrass, smooth brome, and alfalfa. However, sparse distribution, low biomass production, and poorly suited growth habit for harvesting of western mountain aster combined with steep slopes and rocky ground surfaces make phytoremediation using this species an unlikely remediation method.

Introduction

Phosphate mining operations in the Permian Phosphoria Formation in southeast Idaho produces waste rock (shale, limestone, dolostone, chert) subsequently placed in large dumps often as cross-valley fill material. Mixed plant communities are established on the dumps to provide vegetative cover to control erosion. Although many plant species were used in original revegetation seed mixtures, current waste rock dump vegetative cover is mostly a tri-culture of western wheatgrass (*Pascopyrum smithii* (Rydb.)), smooth bromegrass (*Bromus inermis* (Leyss.), and alfalfa (*Medicago sativa* L.) (Chambers and others 1994).

Both the waste rock and associated vegetative cover contain elevated levels of selenium (Se) and other trace elements. The elevated Se levels in waste rock plant communities pose a grazing hazard to native ungulates and livestock (Mackowiak and others 2004).

Selenium concentrations in plants growing on seleniferous soils display a wide range of values depending on lifeform, genus, and species. Certain plant genuses and individual species are known to accumulate large concentrations of Se, sometimes exceeding 1% of plant tissue dry weight. Rosenfeld and Beath (1964) were the first to systematically categorize plant species according to their capacity to absorb Se. Mayland and others (1989) summarized the Se accumulating capacity of plant genuses and species grown on seleniferous soils based on data from Rosenfeld and Beath (1964) and Shrift (1973). We summarize that information in table 1. We use the term, hyperaccumuator, to refer to the primary Se indicator plants as termed by Rosenfeld and Beath (1964). We refer to secondary Se absorbers as accumulators and use the

term excluders for those plant species that do not tend to take up little Se when grown on seleniferous soils. Nonaccumulators are plants that take up only low to moderate amounts of Se from seleniferous soils. The concentration ranges for the different categories of plant Se uptake are suggested approximations. Recently, White and others (2007) extended the definition of 'Se-accumulator' plants to include not only the criteria of high leaf Se concentrations but also very high leaf Se to S ratios. That is, true Se accumulators also take up Se in preference to S.

Phytoremediation is a process by which plants are used to remove excess levels of plant-available contaminants in the rooting zone (e.g., Terry and Banuelos 1999). With phytoremediation, plants take up large amounts of a contaminant, the plants are harvested, and are incinerated or otherwise disposed of in a hazardous waste landfill where the contaminant can be concentrated and isolated from the broader environment. Repeated cropping may be necessary to deplete contaminant levels to where environmental risk is greatly decreased. In the case of Se, the goal of phytoremediation is to deplete plant-available Se in the rooting zone to low-level risk levels to grazing ungulates.

Selenium accumulators have potential to be used for Se phytoremediation of seleniferous waste rock dumps provided 1) plant communities can be established and maintained on waste rock dumps, 2) sufficient biomass can be produced for harvesting and removal, and 3) plant-available Se levels in the rooting zone can be depleted for substantial periods of time (e.g., years to decades).

Unfortunately, most of the commonly known Se-accumulators are either largely absent from southeast ID or are very minor components of the vegetation communities

on the dumps. The western wheatgrass – smooth brome – alfalfa triculture that dominates the waste rock dumps of southeast ID has effectively inhibited plant community diversity. All other species are only minor components on the dump landscapes.

A visual survey of a representative cross-section of waste rock dumps reveals that there are significant areas of the dumps with black shale on the dump surface with little to no vegetation decades after the dumps were established. Low pH (from high levels of Zn sulfides), elevated levels of Ni, Zn, and other elements, low water-holding capacity, and high summertime surface temperatures all combine to inhibit plant species volunteers.

The unit 4 waste rock dump at Wooley Valley (Mackowiak and others 2004) has higher overall measured soil and plant Se levels compared to Champ Mine, Mountain Fuel, and North Maybe Canyon waste rock dumps (Mackowiak and Amacher 2006a,b; unpublished data from North Maybe Canyon). Western mountain aster (*Symphyotrichum spathulatum* (Lindl.) formerly known as *Aster occidentalis* (Nutt.)) is the only Se-accumulator species we have found occupying a significant areal extent on a phosphate mine waste rock dump (Wooley Valley unit 4) and even here it is a minor areal component (< 1 % total dump area) compared to majority of the dump occupied by western wheatgrass, smooth brome, and alfalfa. The largest aster community is found on the terrace of lift 3 with a smaller community on the terrace of lift 2. Within these small-extent plant communities, western mountain aster is the dominant and often the only plant species. Soil conditions may be inhibiting establishment of other plant species or there is some allelopathic effect from the aster.

Another member of the aster family, common woolly sunflower (*Eriophyllum lanatum* (Pursh)), is found widely scattered on the dump and on the edges of the wetland below the dump. Scattered volunteers of hoary tansyaster (*Machaeranthera canescens* (Pursh)) are also found on the dump, but a community of this species is not established anywhere on the dump.

Because western mountain aster is a Se-accumulator and a community of measurable though minor areal extent is found on the dump, we sampled and measured biomass and Se concentrations in the only part of the dump where this species is dominant to determine its potential for phytoremediation of the waste rock dump.

Methods

Site Description

Wooley Valley unit 4 waste rock dump is located at an elevation of about 7000 ft in the headwaters of Angus Creek, which flows into the Blackfoot River. A natural wetland is located at the base of the dump. Dump drainage waters flow through the wetland and several abandoned beaver ponds until they reach a small reservoir at the head of Angus Creek.

The dump was constructed in 4 lifts consisting of north-facing slopes and wide terraces. An open trench is on the east side of the dump and an access road is on the west. Dump material consists of non ore-grade phosphatic shale, middle-waste shale of the Meade Peak Member of the Permian Phosphoria Formation, and discarded limestone and chert units.

The entire dump occupies an area of about 84 acres and was planted with a commonly-used vegetation seed mixture for mine dump revegetation in the 1980s. At present, the plant community on the dump is primarily a tri-culture of western wheatgrass, smooth bromegrass, and alfalfa with scattered volunteer species including western mountain aster.

Plant Sampling

The largest aster community is found on the terrace of lift 3 with a smaller community on the terrace of lift 2. Within these small-extent plant communities, western mountain aster is the dominant and often the only plant species.

An initial survey was conducted in 2003 by sampling widely-scattered western mountain aster and woolly sunflower specimens to determine if these species are accumulating high concentrations of Se at this location. For comparison, three legume species (lupine, sanfoin, and alfalfa) found near the asters were also sampled. The presence or absence of surficial black shale was also noted. Whole plants were clipped to ground level, placed in labeled paper bags, and transported to the laboratory for processing and analysis.

A more detailed survey of the aster stands on the terraces of lifts 2 and 3 was conducted in 2005. Random transects were established through the stands. Because the asters are so sparsely distributed, any significant clumps of asters were sampled after noting distance along the transects. At each sample point, whole plants were clipped to ground level, placed in paper bags, and transported to the laboratory for processing and analysis.

In 2009, selected sample points from the 2005 survey were re-sampled for total above-ground biomass. A 0.5-m^2 quadrat (constructed from PVC pipe and elbow connectors) was placed at each selected sample point and all above-ground aster plants within the quadrat were harvested to ground level and placed in labeled paper bags. The plant samples were returned to the lab for processing.

As part of our assessment of the distribution of Se in legacy waste rock dumps, we sampled dominant plant species for biomass and Se concentrations at Wooley Valley unit 4 in 2002 (Se data summarized in Mackowiak and others 2004), selected waste rock dumps at Champ and Mountain Fuel Mines in 2003 (Mackowiak and Amacher 2006a,b), and selected waste rock dumps at North Maybe Canyon in 2003 and 2004

(unpublished data). Biomass and plant Se concentrations at the four mines were sampled using a random-start, equal-increment transect method. All biomass at each sample point was clipped by lifeform for subsequent drying and weighing. Separate composite plant samples for Se analysis were sampled by species (western wheatgrass, smooth brome, and alfalfa) in a 1-m circle around each sample point. This was done because not every quadrat contained each of the three dominant plant species established on the waste rock dumps.

Plant Sample Preparation and Analysis

Plant samples were dried in mechanical convection ovens at 60 C for 48 h, weighed, and ground to <20-mesh in a Willey mill before digestion. The HNO_3 + H_2O_2 digestion method of Jones (1989) was used to digest plant samples prior to analysis. Selenium in the digests was determined by hydride atomic absorption spectrophotometry (HG-AAS). To convert oxidized Se in the digests to Se(IV) for hydride analysis, equal volumes of digest and concentrated HCl were heated for 20 min at 80 C in a graphite block digester. Conversion efficiency was monitored by carrying a Se(VI) standard through the procedure. Also, several digest samples were spiked with known amounts of Se(IV) and Se(VI) and carried through the Se species conversion procedure. Reagent and method blanks, calibration standards, and check samples were also included as part of the lab QA/QC procedures.

Results and Discussion

Five specimens of western mountain aster were sampled in the initial 2003 survey and all five had Se concentrations in excess of 1000 mg/kg (table 2). Surficial black shale was observed in the areas where the asters were sampled. Although black shale was present in the area where the sanfoin and alfalfa were sampled, Se concentrations in these two legumes, while high, were an order of magnitude less than that found in aster. Black shale was not found at the dump surface in areas where one of the woolly sunflower specimens and lupine were collected and these two species had far less Se than the sanfoin, alfalfa, and aster. The woolly sunflower specimen collected where surficial black shale was noted contained more Se (82.4 mg/kg) than another specimen collected where no black shale was observed (4.9 mg/kg). Selenium results for a more extensive sampling of forbs and legumes are reported in Mackowiak and others (2004). This initial survey established that western mountain aster is a Se accumulator from shales on phosphate mine waste rock dumps compared to a few selected other lifeform specimens collected from the same areas.

The more detailed transect sampling of western mountain aster in 2005 showed that there is considerable spatial variation in Se concentrations in this species (table 3). The large spatial distribution of plant Se concentrations has been observed for other species at Wooley Valley unit 4 waste rock dump (Mackowiak and others 2004). Nevertheless, all but two specimens of aster had Se concentrations in excess of 1000 mg/kg and several specimens exceeded 5000 mg/kg of Se. The mean Se concentration for all aster samples collected in 2005 was 3215 ± 316mg/kg, far in excess of that observed for any other species sampled at unit 4 (Mackowiak and others 2004).

Western mountain aster is sparsely distributed on Wooley Valley unit 4 waste rock dump even in those small areas where it tends to predominate. It also has a compact narrow growth habit at this location with small narrow leaves at the plant crown just above the soil surface and flower stems rarely exceeding 10-15 cm in height. Individual plants are small overall at this location. This growth habit makes it a poor candidate for phytoremediation.

Despite the low biomass, we decided to re-sample the aster transects in 2009 for both biomass and Se concentration to estimate total above-ground plant biomass Se. In 2009, we sampled only the aster community of largest areal extent on lift 3 terrace. Because of the sparse distribution of aster, we did not sample a quadrat at each transect sample point. Instead, we sampled representative sample points with enough aster biomass to produce a viable sample size for analysis (table 4). Aster biomass ranged from 60 to over 300 kg/ha with a mean of 192 ± 24 kg/ha (table 4). Although biased, this sampling represents the maximum biomass per unit area found at this location. To obtain a true statistical sampling of biomass per unit area, a grid of sample points would need to be established, but many of these would show little to no aster present.

Selenium concentrations in aster in 2009 greatly exceeded those found in 2005 at the same sample points (table 4) indicating considerable year to year variation in the Se content of aster should be expected. In 2009, mean Se concentration in aster was 8258 ± 1255 mg/kg, about 2.5 times that found in 2005. Two quadrats had Se concentrations in excess of 1% Se in above-ground aster biomass making this species a clear Se hyperaccumulator from phosphate mining industry waste shale.

The difference in Se concentrations between 2005 and 2009 may in part reflect sampling protocol differences. In 2005, several specimens around each sample point were collected to provide sufficient sample for analysis. In 2009, all aster within the 0.5-m^2 quadrat boundary at each sample point was collected. Thus, more plants per unit area were sampled in 2009. Year to year differences may also reflect changes in growing conditions. The 2009 growing season had a very wet spring so more Se may have been mobilized for uptake by the asters. The 2005 growing season was dry and there may have been less root interception of less plant-available Se mass per unit volume of soil.

The mass of Se in the above-ground biomass of western mountain aster is shown in the last column of table 4. On average, aster has removed and stored in above-ground biomass about 1.5 kg of Se per hectare in those areas where aster is relatively concentrated. Despite the relatively low biomass of aster, the mass of Se in aster is much greater than that in above-ground biomass of grasses (chiefly western wheatgrass and smooth brome) and alfalfa (table 5).

As part of our assessment of the distribution of Se in legacy waste rock dumps, we sampled dominant plant species for biomass and Se concentrations at Wooley Valley unit 4 in 2002 (Se data summarized in Mackowiak and others 2004), selected waste rock dumps at Champ and Mountain Fuel Mines in 2003 (Mackowiak and Amacher 2006a,b), and selected waste rock dumps at North Maybe Canyon in 2003 and 2004 (unpublished data). Average biomass for grasses at all waste rock dumps for all four mines was 926 ± 278 kg/ha whereas for alfalfa it was 1679 + 597 kg/ha. Thus, grasses produce about 5 times the amount of biomass as aster and alfalfa almost 9 times the

amount of biomass as aster. Because mean Se concentrations in grasses and alfalfa (table 5) are much less by 1 - 2 orders of magnitude than Se in aster (table 4), total Se uptake by grasses and alfalfa is significantly less than that accumulated by aster (tables 4 and 5) by a factor of about 29x. To obtain estimated Se mass in grasses and alfalfa in table 5, mean grass and alfalfa biomass was multiplied by mean lifeform Se concentration at each mine.

Feasibility of using aster for phytoremediation of plant-available Se

The high concentrations of Se in western mountain aster (0.1 to more than 1 % of plant dry matter) show that this species is a true Se hyperaccumulator in phosphatic shale. Aster can potentially accumulate about 1540 g/ha of bioavailable Se whereas alfalfa, which has the highest overall biomass of all species on phosphate waste rock dumps (average of 1679 kg/ha for all assessed mines) and removes more Se than grasses, was only able to accumulate about 53 g/ha Se (average for all assessed mines).

However, to be an effective phytoremediation agent, aster distribution and biomass per unit area would need to be increased on the waste rock dumps to the point where it can be harvested and removed. Aster is presently only sparsely distributed and existing grasses and alfalfa would tend to out-compete aster establishment. Grasses and alfalfa would need to be removed by herbicide treatment and aster would need to be heavily seeded to promote establishment. Considerable seedbed preparation is also needed to remove surface rocks and other coarse fragments that currently prevent harvesting by cutting. A 1- 2 in soil layer to produce a smoother growing medium surface and provide

a better germinating environment for aster would also be needed following herbicide treatment and prior to seeding of aster.

The growth habit and non-uniform density of aster distribution does not make this a suitable species for forage harvesting via mowing and bailing. Also, tolerance to cutting, annual re-growth following harvesting, and stand re-establishment vigor are all unknown factors. To deplete plant-available Se within the aster rooting zone, more than one harvest may be needed. Also, the effective depth of the Se extraction zone by the aster root mass on waste rock dumps is unknown. Although promising in terms of hyperaccumulation of Se, phytoremediation of Se on waste rock dumps by aster is likely not feasible at present given its sparse distribution, a growth habit that is not conducive to harvesting, and waste rock dump steep slopes and rocky surfaces that preclude cutting by conventional hay cutting equipment. Attempts to burn aster in the fall have also proven fruitless since the species stays green until very late in the year and is too sparsely distributed to carry fire. In test burns, we were unable to get aster to ignite.

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Table 1--Plant genus or species classified as Se hyperaccumulators (primary indicators), accumulators (secondary Se absorbers), nonaccumulators, and excluders when grown on seleniferous soils. List summarized from Mayland and others (1989) and based on information in Rosenfeld and Beath (1964) and Shrift (1973).

Hyperaccumulators > 500 mg/kg Se	Accumulators 50-100 mg/kg Se	Nonaccumulators < 50 mg/kg Se	Excluders <10 mg/kg Se
Astragulus spp.	*Aster spp.*	Most grain crops	*Trifolium repens* L. (white clover)
Haplopapus spp.	*Astragulus* (some species)	Most grasses	*Buchloe dactyloides* [Nutt.] Engelm. (buffalograss)
Machaeranthera spp.	*Atriplex spp.*	Many forbs	*Bouteloua spp.* (gramagrass)
Stanleya spp.	*Brassica spp.* *Castilleja spp.* *Grindelia spp.* *Gutierrezia spp.* *Machaeranthera* (some species) *Mentzelia spp.*		

Table 2--Se concentrations in selected plant species sampled on 09/04/2003 from various locations on Wooley Valley Unit 4 waste rock dump.

Plant lifeform	Plant species	Location on dump	Surficial black shale	Latitude	Longitude	Plant Se
				deg		mg/kg
Forb	*Eriophyllum lanatum*	Lift 2 terrace	Present	42.817705	-111.394433	82.4
Forb	*Eriophyllum lanatum*	Lift 4 terrace	Absent	42.81616	-111.391206	4.9
Legume	*Lupinus alpestris* (lupine)	Lift 3 terrace	Absent	42.817821	-111.393603	6.0
Legume	*Lupinus alpestris* (lupine)	Lift 3 terrace	Absent	42.817733	-111.39366	30.9
Legume	*Onobrychis viciifolia* (sanfoin)	Lift 2 terrace	Present			185
Legume	*Medicago sativa* (alfalfa)	Lift 4 terrace	Present			586
Forb	*Symphyotrichum spathulatum*	Lift 2 terrace	Present			1998
Forb	*Symphyotrichum spathulatum*	Lift 2 terrace	Present	42.817699	-111.394433	5912
Forb	*Symphyotrichum spathulatum*	Lift 3 terrace	Present	42.81718	-111.392446	2710
Forb	*Symphyotrichum spathulatum*	Lift 3 terrace	Present	42.817463	-111.39225	4049
Forb	*Symphyotrichum spathulatum*	Lift 4 terrace	Present	42.817155	-111.390777	3722

Table 3--Se concentrations in western mountain aster at various locations in two isolated populations sampled on 09/15/2005 at Wooley Valley Unit 4 waste rock dump.

Location on dump	Sample site identification	Transect bearing deg	Distance along transect m	Plant Se mg/kg
Lift 2 terrace	1-1		1.3	276
	1-2		8.0	3795
	1-3		14.7	2970
Lift 3 terrace	2-1	310	0.6	5247
	2-2		7.1	2207
	2-3		13.6	6290
	2-4		20.1	2050
	3-1	290	7.6	3751
	3-2		16.0	4046
	3-3		24.4	3218
	3-4		32.8	2371
	3-5		41.2	2347
	4-1	330	2.0	2200
	4-2		8.8	4102
	4-3		15.6	3631
	4-4		22.4	2188
	4-5		29.2	5433
	5-1	310	7.1	1751
	5-2		15.0	3007
	5-3		22.9	2376
	5-4		30.8	5317
	5-5		38.7	1740
	5-6		46.6	1795
	5-7		54.5	5992
	5-8		62.4	514
Lift 4 slope				4976
			mean ± std err	3215 ± 316

Table 4--Se concentrations and mass at various locations in an isolated population of western mountain aster sampled on 09/24/2009 at lift 3 terrace of Wooley Valley Unit 4 waste rock dump.

Sample site identification	Transect bearing deg	Distance along transect m	Aster biomass kg/ha	Aster Se mg/kg	Aster Se mass g/ha
2-2	310	7.1	60.4	7582	458
2-4		20.1	73.6	5509	405
3-1	290	7.6	192.8	17475	3369
3-3		24.4	332.6	5735	1907
3-5		41.2	197.2	5341	1053
4-2	330	8.8	149.2	16187	2415
4-3		15.6	165.4	9561	1581
4-5		29.2	325.4	6939	2258
5-2	310	15.0	228.0	4223	963
5-3		22.9	164.8	4159	685
5-4		30.8	172.4	7565	1304
5-7		54.5	236.2	8821	2083
		mean ± std err	191.5 ± 24.0	8258 ± 1255	1540 ± 259

Table 5-- Mean ± std err Se concentrations and mass in grasses (*Pascopyrum smithii* and *Bromus inermis*) and alfalfa (*Medicago sativa*) at Champ, Mountain Fuel, North Maybe Canyon, and Wooley Valley (unit 4) waste rock dumps (numbers of samples shown in parentheses).

Location	Year sampled	Lifeform	Predominant plant species	Plant biomass kg/ha	Plant Se mg/kg	Plant Se mass g/ha
Champ mine	2003	Grass	Western wheatgrass Smooth brome	727 ± 74 (n = 68)	6.6 ± 0.8 (n = 150)	4.8
		Legume	Alfalfa	3422 ± 432 (n = 51)	18.6 ± 3.4 (n = 87)	63.6
Mountain Fuel	2003	Grass	Western wheatgrass Smooth brome	305 ± 30 (n = 44)	8.7 ± 1.7 (n = 100)	2.7
		Legume	Alfalfa	1044 ± 221 (n = 25)	56.6 ± 12.6 (n = 50)	59.1
North Maybe Canyon	2003 & 2004	Grass	Western wheatgrass Smooth brome	1622 ± 101 (n = 88)	2.6 ± 0.9 (n = 175)	4.2
		Legume	Alfalfa	1457 ± 154 (n = 71)	9.7 ± 3.5 (n = 90)	14.1
Wooley Valley (unit 4 only)	2002	Grass	Western wheatgrass Smooth brome	1049 ± 61 (n = 96)	25.1 ± 4.5 (n = 121)	26.3
		Legume	Alfalfa	794 ± 108 (n = 96)	96.1 ± 17.6 (n = 59)	76.3
All mines	2002 - 2004	Grass	Western wheatgrass Smooth brome	926 ± 278 (n = 296)	10.8 ± 4.9 (n = 546)	9.5 ± 5.6
		Legume	Alfalfa	1679 ± 597 (n = 243)	45.2 ± 19.8 (n = 286)	53.3 ± 13.6